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Nonlinear Rheology of Confined Polymer Melts under Oscillatory Flow

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ABSTRACT: We present a theory for nonlinear dynamics of confined polymer melts under oscillatory flow. Using a Rouse-like model of chains with finite extensibility, we calculate elastic and dissipative stresses and corresponding storage and loss moduli. The effect of bridges and surface slip are taken into account. Several features have been discovered: the storage modulus G' passes through a maximum with increasing strain amplitude in the range of intermediate frequencies, when adsorption is weak and surface slip is important; the elastic σ' and dissipative σ'' stresses and the corresponding moduli G' and G'' show a jump with increasing strain amplitude when polymer bridges between the surfaces are formed.

I. Introduction

The problem of friction and lubrication at the molecular level attracts significant fundamental and practical interest. A number of papers are devoted to this problem, in particular to the nanorheology of confined polymer melts.[1−14] Confined polymer liquids show some features that are different from those of polymer liquids in the bulk. They show extremely large relaxation time even in the regime of rather short polymer chains which cannot create entanglements. Confined polymer liquids also show nonlinear behavior for much smaller shear rates than in the bulk. Experiments show that the effect of the surfaces on the rheology becomes dominant in the confined state.

A simple model to describe nonlinear rheology of confined polymer melts for steady flow has been developed recently.[12−14] It is based on the Rouse model, but also accounts for a finite extensibility of polymer chains. Two different situations have been considered. The first case corresponds to bulk behavior,[12] when the polymer chains cannot create bridges between the surfaces (the distance between surfaces, h, exceeds the size of the polymer coil, R_G, $h > R_G$). Here, the result of the finite chain extensibility is shear thinning in the regime of high shear rates $\dot\gamma$. In this regime the zero-shear viscosity decreases as $\dot\gamma^{-2/3}$ and this behavior is universal: it does not depend on the details of the chain model. The second case corresponds to a confinement, where the polymer chains create bridges between the surfaces. In the last case, depending on the interaction between the polymer and the surface, several regimes were identified.[13,14]

In the present paper, we further develop our theory for oscillatory flow. Both situations without and with bridges are considered. The organization of the paper is as follows. In the second section, we consider linear and nonlinear behavior of the system without bridges for the strong and weak adsorption limits. In the third section, the effect of bridges is taken into account. In the last section, a discussion of our results is given.

The model used is the following. The polymer chains consist of N statistical segments of length a and excluding volume v, the contour length of the chain is $R_{max} \sim aN$. The friction coefficient of a segment is ζ_0. The imposed flow is characterized by an oscillating strain

$$\epsilon(t) = \epsilon_0 \sin(\omega t) \tag{1}$$

and the strain rate is given by

$$\dot\epsilon(t) = \omega\epsilon_0 \cos(\omega t) \tag{2}$$

with amplitude value $\dot\epsilon_0 = \omega\epsilon_0$. We assume also that the flow is directed along the x axis, and the flow gradient along the z axis.

Our aim is to calculate the storage modulus (G') and the loss modulus (G'').[15−17] This coefficients depend in general on both the frequency ω and the strain amplitude ϵ_0 and are defined in the following way.[18,19] The imposed flow causes nonlinear response of the polymer melt, so that the tangential stress $\sigma(t)$ contains not only the input frequency but also higher order harmonics. The stress can be represented as a Fourier series

$$\sigma(t) = \sum_{k=1,\text{odd}} (\sigma_k'(\epsilon_0,\omega) \sin(k\omega t) + \sigma_k''(\epsilon_0,\omega) \cos(k\omega t)) \tag{3}$$

Due to the isotropy of the polymer melt, this series contains only odd harmonics. Thus, nonlinear response is characterized by the coefficients $\{\sigma_k'(\epsilon_0,\omega), \sigma_k''(\epsilon_0,\omega)\}$, where $k = 1, 3, 5, ...$ The coefficients $\sigma_1'(\epsilon_0,\omega)$ and $\sigma_1''(\epsilon_0,\omega)$ correspond to the elastic and dissipative part of the tangential stress. They are related to the stress $\sigma(t)$ by means of the Fourier transforms

$$\sigma_1'(\epsilon_0,\omega) = \frac{\omega}{2\pi\epsilon_0}\int_0^{2\pi/\omega}\sigma(t)\epsilon(t)\,dt, \quad \sigma_1''(\epsilon_0,\omega) = \frac{1}{2\pi\epsilon_0}\int_0^{2\pi/\omega}\sigma(t)\dot\epsilon(t)\,dt \tag{4}$$

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The storage and loss moduli can be determined in the usual way and are given by

$$G'(\epsilon_0,\omega) = \sigma_1'(\epsilon_0,\omega)/\epsilon_0, \quad G''(\epsilon_0,\omega) = \sigma_1''(\epsilon_0,\omega)/\epsilon_0 \quad (5)$$

The effect of walls on the rheological behavior can be taken into account by the surface friction coefficient ζ_1 for the polymer segments located in a thin surface layer of thickness $\sim a$.[14] When one of the surfaces moves with respect to the other surface with permanent velocity u, the polymer slips near the surfaces with a velocity u_s. The surface slip velocity u_s is defined by the requirement that the surface stress, σ_1,

$$\sigma_1 \sim u_s\zeta_1 a/v \quad (6)$$

is equal to the stress, σ_2, inside the layer

$$\sigma_2 \sim (u - 2u_s)\zeta_0 N(a/h)(a/v) \quad (7)$$

The surface slip velocity therefore is given by

$$u_s \sim \frac{u}{2 + \tau_1 h/\tau_0 aN} \quad (8)$$

where $\tau_1 \sim \zeta_1 a^2$ and $\tau_0 \sim \zeta_0 a^2$ are the segmental relaxation times near the surfaces (τ_1) and far away from them (τ_0) (here and below k_BT is considered as unit energy). Obviously, when $\tau_1 h/\tau_0 aN \ll 1$, surface slip is large, $u_s \sim u/2$, which corresponds to weak adsorption. The other limiting case, $\tau_1 h/\tau_0 aN \gg 1$, corresponds to strong adsorption and the surface slip is small. Similarly we can separate weak and strong adsorption for the situation when $h < aN^{1/2}$ simply by replacing N by the number of segments of the largest unperturbed blob $g_h \sim (h/a)^2$. In this case, the weak adsorption limit is realized for $\tau_1 a/\tau_0 h \ll 1$ and the strong adsorption limit for $\tau_1 a/\tau_0 h \gg 1$. We will assume throughout that $\tau_1/\tau_0 > 1$.

II. Rheology in the Bulk

A. Strong Adsorption Limit. 1. Linear Regimes. Our consideration starts with the linear situation, where the rate of deformation is not too large and the finite extensibility of the polymer chains is not essential. Analytically this condition is defined below. Under those conditions, our model reduces to the standard Rouse model and we first reproduce the basic results for this model in this section. The surface slip is assumed to be small.

Two regimes are identified. The first regime (regime 1.a) corresponds to the low-frequency limit, $\omega\tau_0 N^2 \ll 1$ ($\tau_0 N^2 = \tau_R$ is the Rouse relaxation time). The second regime (regime 2.a) is realized for higher frequencies ($N^{-2} \ll \omega\tau_0 \ll 1$). For very high frequencies ($\omega\tau_0 \gg 1$) the response is determined by a monomeric scale and thus the polymer nature of the liquid is not important in this regime which will not be considered further here.

In the first regime, the situation is close to the steady (equilibrium) state and the dissipative response is dominant. The loss modulus is given by

$$G'' \sim \omega\eta \sim \omega\tau_0 N/v \quad (9)$$

where $\eta \sim \tau_0 N/v$ is the bulk linear viscosity.[15,16] The storage modulus G' is connected with the phase difference δ between the strain and the stress

$$G' \sim \tan^{-1}(\delta) G'' \quad (10)$$

Taking into account that $\tan\delta \sim (\omega\tau_R)^{-1}$,[15,17] we find that

$$G' \sim (\omega\tau_0)^2 N^3/v \quad (11)$$

The next regime (regime 2.a) corresponds to higher frequencies ($N^{-2} \ll \omega\tau_0 \ll 1$). In order to investigate this regime let us divide the chain into blobs, each of which has g segments. During the period of oscillations, the maximum blob $g = g_0$ which comes to equilibrium is determined by the condition $\omega\tau_B \sim 1$, where $\tau_B = \tau_0 g_0^2$ is the blob relaxation time, so that $g_0 \sim (\omega\tau_0)^{-1/2}$. The chains cannot relax on scales larger than g_0 (as the corresponding relaxation time $\gg 2\pi/\omega$), and therefore, the blobs contribute to the stress nearly independently. The storage and loss moduli thus only depend on the frequency in this regime and not on N, $G' = f'(\omega\tau_0)/v$, or $G'' = f''(\omega\tau_0)/v$ and can be calculated using a scaling approach. Recalling that for $(\omega\tau_0) \sim N^{-2}$ these moduli must crossover with regime 1.a, $G' \sim G'' \sim N^{-1}$, and imposing a scaling frequency dependence of the moduli we get

$$G' \sim G'' \sim (\omega\tau_0)^{1/2}/v \quad (12)$$

We thus recover the principle results for the Rouse model:[15-17] for low frequencies ($\omega\tau_0 N^2 \ll 1$) $G' \sim (\omega\tau_0)^2$, $G'' \sim (\omega\tau_0)$, and for high frequencies ($N^{-2} \ll \omega\tau_0 \ll 1$) $G' \sim G'' \sim (\omega\tau_0)^{1/2}$.

2. Nonlinear Regimes. In this section we consider the nonlinear case, where the strain amplitude is large and the finite extensibility becomes important. The starting point of our consideration is to define the relaxation times of the chain. Let us assume that the frequency is low and the situation is close to the steady state. As was shown in the previous paper,[12] the flow compresses the chain in the normal direction due to the mechanism of finite extensibility. The normal size of the chain is $R_n \sim \xi < aN^{1/2}$. The parameter ξ depends on the strain rate $\epsilon_0\omega$ and is given by[12]

$$\xi \sim a(\epsilon_0\omega\tau_0)^{-1/3} \quad (13)$$

Obviously, $\xi < R_G \sim aN^{1/2}$ if $\epsilon_0\omega > \tau_0^{-1}N^{-3/2}$. The characteristic value of the x component of the end-to-end vector is $R_x \sim aN$; therefore, the conformation of the chain is highly anisotropic. Due to this anisotropy, the chain relaxation is in principle characterized by two different relaxation times, $\tau_\parallel$ and $\tau_\perp$. The first time can be defined as the displacement time of the chain under the flow along the axis x over a distance comparable to its own size $R_x \sim aN$ and is given by (the characteristic velocity is $V \sim \epsilon_0\omega R_n$)

$$\tau_\parallel \sim \frac{aN}{V} \sim \frac{aN}{\epsilon_0\omega\xi} \sim N\tau_0(\epsilon_0\omega\tau_0)^{-2/3} \quad (14)$$

The second time is the diffusion time corresponding to a diffusion over a distance $\sim\xi$ in the normal direction and equals

$$\tau_\perp \sim N\zeta_0\xi^2 \sim N\tau_0(\epsilon_0\omega\tau_0)^{-2/3} \quad (15)$$

Obviously these two times are of the same order:

$$\tau_{\parallel} \sim \tau_{\perp} \sim \tau^* \sim N\tau_0(\epsilon_0\omega\tau_0)^{-2/3} \tag{16}$$

so that the nonlinear regime can in fact be characterized by a single relaxation time τ^*. This relaxation time is obviously smaller than the Rouse relaxation time $\tau_R = \tau_0 N^2$, which implies an enhancement of the relaxational processes in the nonlinear regime. The condition $\xi \sim aN^{1/2}$ determines the boundary between the linear and nonlinear low-frequency regimes

$$\epsilon_0 \sim (\omega\tau_0)^{-1}N^{-3/2} \tag{17}$$

Furthermore, the condition $\omega\tau^* \sim 1$ gives the crossover between the low- and high-frequency limits. The crossover frequency is thus

$$\omega^* \sim \epsilon_0{}^2 N^{-3}/\tau_0 \tag{18}$$

The first nonlinear regime (regime 3.a) corresponds to the low frequencies ($\omega \ll \omega^*$). The storage and loss moduli can be calculated similarly to for regime 1.a as the situation is close to the steady state. The viscosity in the nonlinear steady case has been calculated in ref 12, $\eta \sim (\epsilon_0\omega\tau_0)^{-2/3}/\nu$; therefore, the loss modulus is

$$G'' \sim \omega\eta \sim \epsilon_0{}^{-2/3}(\omega\tau_0)^{1/3}/\nu \tag{19}$$

The storage modulus can be obtain from eq 10 with $\tan\delta \sim (\omega\tau^*)^{-1}$

$$G' \sim N\epsilon_0{}^{-4/3}(\omega\tau_0)^{2/3}/\nu \tag{20}$$

The next regime (regime 4.a) corresponds to $\omega > \omega^*$. In this case, the whole chain cannot come to the equilibrium state during the period of the oscillations. However, on smaller scales this equilibrium can be attained. The maximum scale on which local equilibrium is attained corresponds to the blob containing g^* segments. This blob size can be found from the condition

$$\omega\tau_{g^*} \sim 1 \tag{21}$$

where τ_{g^*} is the relaxation time of the g^* blob. In the nonlinear situation, this time can be defined similarly to that for the low-frequency limit as a stretching time of the g^* blob in the x direction or as a diffusion time in the normal direction:

$$\tau_{g^*} \sim g^*\zeta_0\xi^2 \tag{22}$$

Using eqs 13, 21, and 22 we obtain

$$g^* \sim \epsilon_0{}^{2/3}(\omega\tau_0)^{-1/3} \tag{23}$$

Similarly as for regime 2.a, the storage and loss moduli can be calculated now using the scaling approach. The moduli do not depend on N and can be represented in the form $G' \propto \epsilon_0{}^{a_1}\omega^{\beta_1}$, $G'' \propto \epsilon_0{}^{a_2}\omega^{\beta_2}$. The lower frequency results imply that for $\omega \sim \omega^*$, $G' \sim G'' \sim N^{-1}$. Thus we get with the "scaling accuracy"

$$G' \sim G'' \sim \epsilon_0{}^{-2/3}(\omega\tau_0)^{1/3}/\nu \tag{24}$$

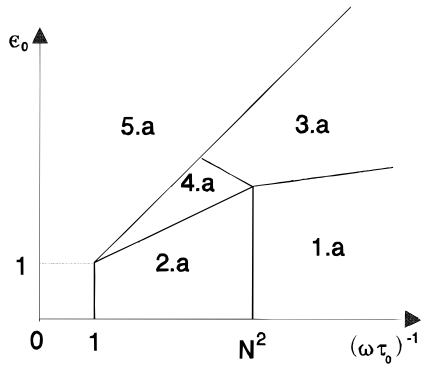

Figure 1. Diagram of regimes in the coordinates $(\epsilon_0; (\omega\tau)^{-1})$ for the strong adsorption limit ($\tau_1/\tau_0 > h/a$, $h > aN^{1/2}$).

Obviously, regime 4.a extends up to the frequency ω^{**} which is defined by the condition $g^* \sim 1$:

$$\omega^{**} \sim \tau_0{}^{-1}\epsilon_0{}^2 \tag{25}$$

For very high frequencies $\omega > \omega^{**}$, a new regime appears. We do not investigate this regime here. The rheology in this regime is governed by the detailed chemical structure of the polymer chains on scales smaller than the size of one link, a.

The boundary between linear high-frequency regime 2.a and nonlinear high-frequency regime 4.a can be found from the condition $g^* \sim g_0 \sim (\omega\tau_0)^{-1/2}$

$$\epsilon_0 \sim \epsilon_0{}^* = (\omega\tau_0)^{-1/4}, \quad N^{-2} \ll \omega\tau_0 \ll 1 \tag{26}$$

So far we considered contributions to the moduli exclusively due to the polymeric nature of the molecules. However, there is an additional mechanism of dissipation, which is due to direct friction between the polymer segments, and which is nearly the same for polymeric and analogous low molecular weight liquids.[20] The viscosity of the system of unconnected links is $\eta_0 \sim \tau_0/\nu$; therefore, its moduli are given by

$$G'' \sim \eta_0\omega \sim \omega\tau_0/\nu, \quad G' \sim (\omega\tau_0)^2/\nu \tag{27}$$

These terms might be important in the nonlinear range (regimes 3.a and 4.a). Thus, in these regimes the loss modulus must be written as

$$G'' \sim \epsilon_0{}^{-2/3}(\omega\tau_0)^{1/3}/\nu + \omega\tau_0/\nu \tag{28}$$

Similarly for the storage modulus. The contribution from the segmental friction is dominant for $\epsilon_0\omega\tau_0 > 1$ (regime 5.a), when the normal fluctuation size of the chain $\xi < a$. We do not consider this regime here. Under this condition, even a low molecular liquid reveals nonlinear behavior.

The whole diagram of the regimes in the coordinates $(\epsilon_0; \Theta \equiv (\omega\tau_0)^{-1})$ is shown in Figure 1. Regime 1.a implies low-frequency linear behavior and is valid in the region $[N^2 < \Theta; \epsilon_0 < \Theta N^{-3/2}]$. The scaling dependences of the storage and loss moduli in this regime coincide with the standard Rouse predictions and are given by

$$G' \sim N^3\omega^2, \quad G'' \sim N\omega \tag{29}$$

Regime 2.a corresponds to linear behavior for high frequencies and occupies the range $[1 < \Theta < N^2; \epsilon_0 <$

$\Theta^{1/4}$]. The storage and loss moduli in this regime also coincide with the Rouse ones

$$G' \sim G'' \sim \omega^{1/2} \tag{30}$$

Regime 3.a is the nonlinear low-frequency regime [$\epsilon_0 < \Theta$; $\epsilon_0^{-2}N^3 < \Theta < \epsilon_0 N^{3/2}$]. In this regime

$$G' \sim N\epsilon_0^{-4/3}\omega^{2/3}, \quad G'' \sim \epsilon_0^{-2/3}\omega^{1/3} \tag{31}$$

Regime 4.a finally represents the nonlinear regime for high frequencies: [$\Theta < \epsilon_0^{-2}N^3$; $\Theta^{1/4} < \epsilon_0 < \Theta$]. The storage and loss moduli in this regime are given by

$$G' \sim \epsilon_0^{-2/3}\omega^{1/3}, \quad G'' \sim \epsilon_0^{-2/3}\omega^{-1/3} \tag{32}$$

B. Weak Adsorption Limit. 1. Linear Regimes. We now proceed to the case when surface slip is important, $(\tau_0 aN)/(\tau_1 h) > 1$, and the distance between the surfaces h still satisfies $h > aN^{1/2}$. Obviously, the surface slip affects the strain rate inside the layer. If the imposed velocity is $u(t) = \dot{\epsilon}(t)h$ and the surface slip velocity is $u_s(t) = \dot{\epsilon}_s(t)h$, where

$$\epsilon_s(t) = \epsilon_s' \sin(\omega t) - \epsilon_s'' \cos(\omega t) \tag{33}$$

(the parameters ϵ_s' and ϵ_s'' are calculated below), then the strain rate inside the layer is $\dot{\epsilon}^*(t) = \dot{\epsilon}(t) - 2\dot{\epsilon}_s(t)$. For the nonlinear situation, higher order harmonics should also be included in the expansion (33). This harmonics are not important for us, however, as we investigate the response on the imposed frequency.

Thus we reduce the problem to a calculation of the quantities ϵ_s' and ϵ_s''. Note that the stress is uniform inside the layer for a given time moment (the inertial effects are small). The stress in the thin surface layer, where the slip takes place is

$$\sigma_1(t) \sim (u_s(t)\zeta_1 a)/v \tag{34}$$

The stress far away from the wall can be calculated using the method of the previous sections. The effective strain inside the layer, $\epsilon^*(t) = \epsilon(t) - 2\epsilon_s(t)$, is

$$\epsilon^*(t) = \epsilon_0 f(x,y) \sin(\omega t + \phi) \tag{35}$$

Here we use the following definitions

$$x = \epsilon_s'/\epsilon_0, \quad y = \epsilon_s''/\epsilon_0,$$

$$f(x,y) = ((1-2x)^2 + 4y^2)^{1/2},$$

$$\tan\phi = 2y/(1-2x) \tag{36}$$

The elastic and dissipative stresses can thus be written as

$$\sigma' = \epsilon_0 f(x,y)(G_a' \cos\phi - G_a'' \sin\phi),$$

$$\sigma'' = \epsilon_0 f(x,y)(G_a' \sin\phi + G_a'' \cos\phi) \tag{37}$$

where the values of the moduli G_a' and G_a'' depend on the amplitude $\epsilon_0 f(x,y)$ and the frequency ω; the moduli G_a' and G_a'' characterize the corresponding regimes in the strong adsorption limit. On the other hand, the elastic and dissipative stresses near the surface can be found from eq 34

$$\sigma_1' \sim \frac{1}{v}\frac{h}{a}\epsilon_0\omega\tau_1 y, \quad \sigma_1'' \sim \frac{1}{v}\frac{h}{a}\epsilon_0\omega\tau_1 x \tag{38}$$

Finally, the system of equations

$$\sigma_1' = \sigma', \quad \sigma_1'' = \sigma'' \tag{39}$$

allows us to calculate the quantities x and y and to find the storage and loss moduli using eqs 5 and 38.

We start with the linear low-frequency limit $\omega < \tau_R^{-1} = (\tau_0 N^2)^{-1}$. Using the moduli G' and G'' for regime 1.a, we rewrite the system of equations (39) in the form

$$\frac{\tau_1 h}{\tau_0 aN}y = (\omega\tau_0 N^2)(1-2x) - 2y,$$

$$\frac{\tau_1 h}{\tau_0 aN}x = (1-2x) + 2(\omega\tau_0 N^2)y \tag{40}$$

Next we find x and y and calculate the moduli:

$$G' = f(x,y)[G_a' \cos\phi - G_a'' \sin\phi] \sim \frac{1}{v}(\omega\tau_1)^2\left(\frac{h}{a}\right)^2 N$$

$$G'' = f(x,y)[G_a' \sin\phi + G_a'' \cos\phi] \sim \frac{1}{v}(\omega\tau_1)\left(\frac{h}{a}\right) \tag{41}$$

This regime is denoted as regime 1.b.

The next regime corresponds to higher frequencies, $\tau_0^{-1}N^{-2} < \omega < \tau_0^{-1}$. The quantities x and y in this case can be obtained from the equations

$$\frac{\tau_1 h}{\tau_0 a}(\omega\tau_0)^{1/2}y = 1 - 2x - 2y$$

$$\frac{\tau_1 h}{\tau_0 a}(\omega\tau_0)^{1/2}x = 1 - 2x + 2y \tag{42}$$

We can actually distinguish two regimes here. Regime 2.b occurs for $(\tau_1 h)^2/(\tau_0 a)^2 < (\omega\tau_0)^{-1} < N^2$. In this case, the surface slip is large ($x \sim 1/2$) and the storage and loss moduli are

$$G' \sim \frac{1}{v}(\omega\tau_0)^{3/2}\left(\frac{\tau_1 h}{\tau_0 a}\right)^2$$

$$G'' \sim \frac{1}{v}(\omega\tau_1)\left(\frac{h}{a}\right) \tag{43}$$

Regime 3.b exists for $(\tau_1 h)^2/(\tau_0 a)^2 > (\omega\tau_0)^{-1} > 1$. Analysis shows that the surface slip is small in this case and the corresponding moduli coincide with those in regime 2.a of the strong adsorption limit, eq 12.

2. Nonlinear Regimes. Now we proceed to the nonlinear regimes and start again with low frequencies, where the moduli are defined by the eqs 19 and 20. The system of equations for x and y is

$$\alpha_1 y = \alpha_2 f^{-4/3}(x,y)(1-2x) - 2y f^{-2/3}(x,y),$$

$$\alpha_1 x = f^{-2/3}(x,y)(1-2x) + 2\alpha_2 f^{-4/3}(x,y)y \tag{44}$$

where

$$\alpha_1 = \frac{\tau_1 h}{\tau_0 a}(\epsilon_0\omega\tau_0)^{2/3}$$

$$\alpha_2 = N\epsilon_0^{-2/3}(\omega\tau_0)^{1/3} \tag{45}$$

This system can be investigated analytically with an additional assumption that

$$(1 - 2x) \gg y, \quad \alpha_2 \ll (1 - 2x)^{2/3} \tag{46}$$

which is checked after these calculations. The first condition implies that the flow inside the layer is nearly in phase with the imposed flow. The second condition can be presented in the form $\omega\tau^* \ll 1$, where $\tau^* \sim \tau_0 N[\epsilon_0 - (1 - 2x)\omega\tau_0]^{-2/3}$ is the relaxation time of the chain. The equation for x is then

$$(1 - 2x)^{1/3} = \alpha_1 x \tag{47}$$

Depending on the parameter α_1, two situations are possible. If this parameter is small, which is true for a small enough strain amplitude, $\epsilon_0 < \epsilon_1$, where

$$\epsilon_1 \sim \left(\frac{\tau_0 a}{\tau_1 h}\right)^{3/2} (\omega\tau_0)^{-1} \tag{48}$$

then the surface slip is important: $x \sim 1/2$. Calculations show that the storage and loss moduli in this case (regime 1.b*) coincide with those obtained in regime 1.b (eq 41). This result is valid for $\omega > \omega_1$, where

$$\omega_1 \sim \tau_0^{-1} N \epsilon_0^{-2} (a\tau_0/h\tau_1)^2 \tag{49}$$

(it results from the second assumption of eq 46). In the opposite case $\epsilon_0 > \epsilon_1$, the surface slip is small and the corresponding regime (regime 4.b) coincides with regime 3.a of the strong adsorption limit. The loss and storage moduli in regime 4.b are given by the eqs 19 and 20. Regime 4.b exists for the frequencies $\omega < \omega_2$, where

$$\omega_2 \sim \tau_0^{-1} N^{-3} \epsilon_0^{\,2} \tag{50}$$

This boundary follows from the condition ($\omega\tau^* \sim 1$). Below we show that the lines $\omega \sim \omega_1$ and $\omega \sim \omega_2$ separate low-frequency and high-frequency regimes (the regimes 1.b, 5.b and 4.b, 6.b, respectively).

Note that high-frequency regimes are determined by the condition $\omega\tau^* \gg 1$. These regimes can be investigated using the moduli G_a' and G_a'' from regime 4.a of the strong adsorption limit (eq 24). The system of equations for x and y has the form

$$\alpha_1 y = f^{-2/3}(x,y)(1 - 2x - 2y), \quad \alpha_1 x = f^{-2/3}(x,y)(1 - 2x + 2y) \tag{51}$$

where α_1 is given by the eq 45. Analysis shows that in this case $(1 - 2x) \sim 2y$. However, the equation for x is still approximately given by eq 47. Here we also can separate a situation with large slip $x \sim 1/2$, when $\epsilon_0 < \epsilon_1$ (regime 5.b), and one with small slip, $\epsilon_0 > \epsilon_1$ (regime 6.b). Calculations show that in regime 5.b the storage and loss moduli are given by

$$G' \sim \frac{\epsilon_0^{\,2}}{\nu} (\omega\tau_0)^3 \left(\frac{\tau_1 h}{\tau_0 a}\right)^4$$

$$G'' \sim \frac{1}{\nu} (\omega\tau_1) \left(\frac{h}{a}\right) \tag{52}$$

Regime 6.b coincides with regime 4.a of the strong adsorption limit eq 24.

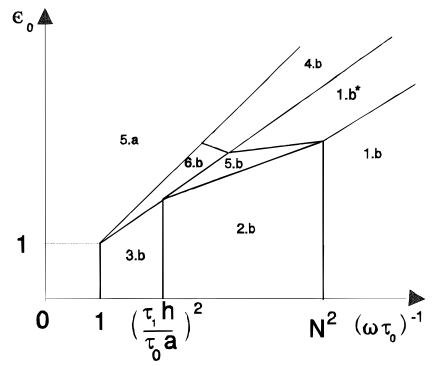

Figure 2. Diagram of regimes in the coordinates (ϵ_0; $(\omega\tau)^{-1}$) for the weak adsorption limit ($\tau_1/\tau_0 < h/a$, $h > aN^{1/2}$).

The last problem is to find the boundaries between the linear and nonlinear regimes (2.b, 5.b and 3.b, 6.b). Requiring a smooth crossover between these regimes we get for the boundaries between the regimes 2.b and 5.b (the first equation in (53)), and regimes 3.b and 6.5 (the second equation in (53))

$$\epsilon_0 \sim (\omega\tau_0)^{-3/4} (\tau_0 a)/(\tau_1 h), \quad (\tau_1 h)^2/(\tau_0 a)^2 < (\omega\tau_0)^{-1} < N^2$$

$$\epsilon_0 \sim (\omega\tau_0)^{-1/4}, \quad 1 < (\omega\tau_0)^{-1} < (\tau_1 h)^2/(\tau_0 a)^2 \tag{53}$$

The boundary between regimes 1.b and 5.b and regimes 4.b and 6.b can be found in a similar way. These boundaries are described by eqs 49 and 50.

The whole diagram of regimes in the coordinate (ϵ_0, $\Theta \equiv (\omega\tau_0)^{-1}$) is shown in Figure 2. The equations of the boundaries are given by

$$\Theta_{b1} = N^2, \quad \Theta_{b2} = \left(\frac{\tau_1 h}{\tau_0 a}\right)^2, \quad \Theta_{b3} = 1, \quad \epsilon_{b1} = \Theta N^{-1/2} \frac{\tau_0 a}{\tau_1 h},$$
$$\epsilon_{b2} = \Theta^{3/4} \frac{\tau_0 a}{\tau_1 h}, \quad \epsilon_{b3} = \Theta^{1/4}, \quad \epsilon_{b4} = \Theta \left(\frac{\tau_0 a}{\tau_1 h}\right)^{3/2},$$
$$\epsilon_{b5} = \Theta^{1/2} N^{1/2} \frac{\tau_0 a}{\tau_1 h}, \quad \epsilon_{b6} = \Theta^{-1/2} N^{3/2}, \quad \epsilon_{b7} = \Theta \tag{54}$$

The scaling dependence of the moduli vs N, ω, ϵ_0 is the following ($\Theta^* = \tau_1 h N/\tau_0 a$)

regime 1.b: $[\Theta > \Theta_{b1}; \quad \epsilon_0 < \epsilon_{b1}]$

$$G' \sim N\omega^2, \quad G'' \sim \omega \tag{55}$$

regime 1.b*: $[\epsilon_{b1} < \epsilon_0 < \epsilon_{b4}$ if $\Theta_{b1} < \Theta$; $\epsilon_{b5} < \epsilon_0 < \epsilon_{b4}$, if $\Theta^* < \Theta < \Theta_{b1}]$

$$G' \sim N\omega^2, \quad G'' \sim \omega \tag{56}$$

regime 2.b: $[\epsilon_0 < \epsilon_{b2}; \quad \Theta_{b2} < \Theta < \Theta_{b1}]$

$$G' \sim \omega^{3/2}, \quad G'' \sim \omega \tag{57}$$

regime 3.b = regime 2.a: $[\epsilon_0 < \epsilon_{b3}; \quad \Theta_{b3} < \Theta < \Theta_{b2}]$

$$G' \sim G'' \sim \omega^{1/2} \tag{58}$$

regime 4.b = regime 3.a: [$\epsilon_{b4} < \epsilon_0 < \epsilon_{b7}$ if $\Theta^* < \Theta$; $\epsilon_{b6} < \epsilon_0 < \epsilon_{b7}$ if $N < \Theta < \Theta^*$]

$$G' \sim N\epsilon_0^{-4/3}\omega^{2/3}, \quad G'' \sim \epsilon_0^{-2/3}\omega^{1/3} \tag{59}$$

regime 5.b: [$\epsilon_{b2} < \epsilon_0 < \epsilon_{b5}$ if $\Theta^* < \Theta < \Theta_{b1}$; $\epsilon_{b2} < \epsilon_0 < \epsilon_{b4}$ if $\Theta_{b2} < \Theta < \Theta^*$]

$$G' \sim \epsilon_0^{2}\omega^{3}, \quad G'' \sim \omega \tag{60}$$

regime 6.b = regime 4.a: [$\epsilon_{b3} < \epsilon_0$ if $\Theta_{b3} < \Theta < \Theta_{b2}$; $\epsilon_{b4} < \epsilon_0$ if $\Theta_{b2} < \Theta < \Theta^*$; $\epsilon_0 < \epsilon_{b7}$ if $\Theta_{b3} < \Theta < N$; $\epsilon_0 < \epsilon_{b6}$ if $N < \Theta < \Theta^*$]

$$G' \sim \epsilon_0^{-2/3}\omega^{1/3}, \quad G'' \sim \epsilon_0^{-2/3}\omega^{1/3} \tag{61}$$

III. Effect of Bridges

A. Linear Regimes. So far the distance between the surfaces was assumed to be much larger than the coil size $h > aN^{1/2}$. Next we investigate the opposite situation, $h < aN^{1/2}$. The important new feature in this case is the presence of polymer bridges between the surfaces. In the limit of low imposed frequency, the bridges are important for high surface friction, $\tau_1/\tau_0 > h/a$.[14] We assume here that the last condition is satisfied. However, if this frequency exceeds the inverse Rouse relaxation time of the bridge, $T_0^{-1} = \tau_0^{-1}(a/h)^4$, the bridges do not have time to come to equilibrium and thus are equivalent to other (nonbridging) chain fragments. We restrict the consideration in this section to the region, where the effect of bridges is crucial, $\omega < \tau_0^{-1}(a/h)^4$.

Let us proceed to the linear regimes. The characteristic relaxation time of the bridges is $T_1 \sim \tau_1(h/a)^3$;[14] therefore, the low-frequency limit corresponds to the frequencies $\omega < T_1^{-1}$ (regime 1.c). The storage and loss moduli in this regime are determined by the surface friction. The friction coefficient per bridge is $\zeta_1^* = \zeta_1 h/a$, and the average surface concentration of the bridges is $\nu_0 \sim a^2/(\nu h)$. Therefore the loss modulus is

$$G'' \sim \nu_0 \omega \zeta_1^* h \sim \frac{1}{\nu}\frac{h}{a}\omega\tau_1 \tag{62}$$

The storage modulus can be expressed through G'' and $\tan\delta \sim (\omega T_1)^{-1}$

$$G' \sim \tan^{-1}\delta G'' \sim \frac{1}{\nu}\left(\frac{h}{a}\right)^4(\omega\tau_1)^2 \tag{63}$$

The next regime (regime 2.c) corresponds to frequencies $\omega > T_1^{-1}$. If the strain amplitude $\epsilon_0 < h/a$, the bridges cannot break during the oscillation period and give an elastic contribution to the stress. The elastic coefficient of the bridges is $\kappa \sim (1/h)^2$, so the storage modulus in this case is given by

$$G' \sim \nu_0 \kappa h \sim \frac{1}{\nu}\left(\frac{a}{h}\right)^2 \tag{64}$$

The loss modulus is expressed through the modulus G'

$$G'' \sim \tan\delta G' \sim \frac{1}{\nu}\left(\frac{a}{h}\right)^5(\omega\tau_1)^{-1} \tag{65}$$

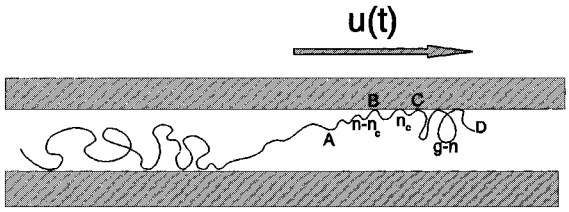

Figure 3. Conformation of the breaking bridge.

However, in the present situation there is an additional important contribution to the moduli from the loops, which also have an average surface concentration of order ν_0. This contribution can be easily calculated. The average friction coefficient of the loop is $\zeta_0^* = \zeta_0(h/a)^2$, therefore the loss modulus is

$$G_1'' \sim \nu_0 h\omega\zeta_0^* \sim \frac{1}{\nu}\left(\frac{h}{a}\right)^2(\omega\tau_0) \tag{66}$$

The relaxation time of the loop is the Rouse time $T_0 = \tau_0(h/a)^4$, so the storage modulus is

$$G_1' = \omega T_0 G_1'' \sim \frac{1}{\nu}\left(\frac{h}{a}\right)^6(\omega\tau_0)^2 \tag{67}$$

Taking into account that in regime 2.c $G' > G_1'$, we can write the final equations for the moduli as

$$G' \sim \frac{1}{\nu}\left(\frac{a}{h}\right)^2, \quad G'' \sim \frac{1}{\nu}\left(\left(\frac{h}{a}\right)^2(\omega\tau_0) + \left(\frac{a}{h}\right)^5(\omega\tau_1)^{-1}\right) \tag{68}$$

B. Nonlinear Regimes. 1. High Surface Friction, $\tau_1/\tau_0 > (h/a)^4$. The nonlinear situation can be investigated based on our previous results.[14] Let us assume that the frequency $\omega < T_1^{-1}$, and the stretching time of the bridges $t^* \sim h^2/(au) < T_1$, where $u = h\epsilon_0\omega$ is the relative velocity between the surfaces. The last condition implies that the bridge breaks due to the finite extensibility of the chain. During the stretching time t^* the bridge forms $\sim g^{1/2}$ contacts with the surface. Here g is the number of segments in the attached blob.[14] The blob g can be found from the condition $t^* \sim \tau_1 g^{3/2}$, where $\tau_1 g^{3/2}$ is the attaching time of the g blob to the surface

$$g \sim (t^*/\tau_1)^{2/3} \sim (h/a\epsilon_0\omega\tau_1)^{2/3} \tag{69}$$

The elongation force, f_t, of the bridge is determined by the surface friction ζ_1 and the number of contacts between the surface and part of attaching g blob containing n_c segments, which is rubbed with the surface (Figure 3). In our previous consideration[14] we assumed that $f_t \sim n_c^{1/2}u\zeta_1$ as in the equilibrium. However, in the dynamical regime this force should be different. Really let us assume that in some intermediate state n segments already pulled from the surface under the force f_t and displaced in the normal direction on the average distance[14]

$$d_{av} \sim a^2 n/h \tag{70}$$

The typical fluctuation displacement of the segments is

$$d_{fl} \sim (an/f_t)^{1/2} \tag{71}$$

Obviously, only a blob of n_c segments which satisfies the condition

$$d = d_{av}(n_c) = d_{fl}(n_c) \tag{72}$$

could be rubbed with the surface. The condition $d > a$ should be obviously fulfilled. The average number of contacts between the rubbing blob and the surface is $\sim an_c/d$; therefore, the average elongation force is

$$f_t \sim (an_c/d)u\zeta_1 \tag{73}$$

Equations 72 and 73 allow us to calculate d, n_c, and f_t. In particular, the elongation force is $f_t \sim (h/a)u\zeta_1$.

The bridge breaks during the time $\tau_b \sim ag/u$; the lifetime of the bridge is t^*, therefore, the average force per one bridge is

$$f_b = f_t\tau_b/t^* \tag{74}$$

Similarly we can consider the case $d = a$ (obviously d cannot be smaller than a). In this situation $n_c \sim g$ (since $g < h/a$), and the elongation force $f_t \sim gu\zeta_1$. The surface blob is broken after it displaces in the normal direction on the distance $\sim a$. The corresponding normal velocity is $v_n = ua/h$; therefore, the break time is $\tau_b \sim a/v_n \sim h/u$. The average force, f_b, transformed by one bridge in this case coincides with that in eq 74.

The average stress can be estimated as[14]

$$\sigma_t \sim \nu_t(g)f_t\tau_b/t^* \tag{75}$$

where $\nu_t(g)$ is the surface concentration of the bridges. This concentration has been calculated in ref 14 using the quasi-equilibrium assumption for the permanent velocity,

$$\nu_t(g) = \nu_0(g) \sim \frac{a}{v}\left(\frac{a}{h}\right)^2 g^{1/2} \tag{76}$$

After substitution of eq 76 in eq 75 we find that the stress is constant and independent of the velocity:

$$\sigma'' \sim (1/v)(a/h) \tag{77}$$

However, when the velocity depends on time, the distribution of the bridges and as a result their surface concentration also depends on time. The simplest way to calculate the surface concentration of the bridges is to write a relaxational equation. The characteristic relaxation time of the bridge is t^*; therefore, any deviation of the surface concentration of the bridges from the quasi-equilibrium $\nu_0(g)$ approximately obeys the relaxational equation

$$\frac{d\nu_t}{dt} = -\frac{1}{t^*}(\nu_t - \nu_0) \tag{78}$$

From here we can calculate elastic part of the stress (the dissipative part is described by eq 77)

$$\sigma' \sim \omega$$
$$t^*\sigma'' \sim (1/v)\epsilon_0^{-1} \tag{79}$$

The loss and storage moduli are given by

$$G'' \sim (1/v)(a/h)\epsilon_0^{-1}, \quad G' \sim (1/v)\epsilon_0^{-2} \tag{80}$$

We denote the considered regime as regime 3.c. The last one is valid, when $1 < g < g_h \sim (h/a)^2$. Taking into account that $g \sim (h^2/au\tau_1)^{2/3}$, we rewrite the last conditions in the form $\epsilon_{c1} < \epsilon_0 < \epsilon_{c2}$, where

$$\epsilon_{c1} \sim \left(\frac{a}{h}\right)^2(\omega\tau_1)^{-1}, \quad \epsilon_{c2} \sim \left(\frac{h}{a}\right)(\omega\tau_1)^{-1} \tag{81}$$

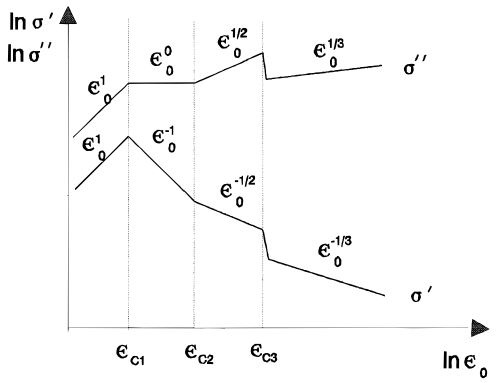

Figure 4. Dependence of the elastic and dissipative stresses vs strain amplitude.

The next nonlinear regime with bridges (regime 4.c) exists for the strain amplitudes $\epsilon_{c2} < \epsilon_0 < \epsilon_{c3}$, where ϵ_{c3} is determined from the condition that the flow strongly affects the chain conformation inside the layer so that bridges cannot be formed any more. This strain amplitude is obtained from eq 17 with $N = (h/a)^2$

$$\epsilon_{c3} \sim \left(\frac{a}{h}\right)^3(\omega\tau_0)^{-1} \tag{82}$$

Now only one segment can penetrate into the surface layer. The dissipative stress in this case was found to be[14]

$$\sigma'' \sim (1/v)(\omega\tau_1\epsilon_0)^{1/2}(a/h)^{3/2} \tag{83}$$

and the elastic stress

$$\sigma' \sim \omega t^*\sigma'' \sim (1/v)(\omega\tau_1/\epsilon_0)^{1/2}(a/h)^{1/2} \tag{84}$$

The loss and storage moduli are given by

$$G'' \sim (1/v)(\omega\tau_1)^{1/2}(a/h)^{3/2}\epsilon_0^{-1/2},$$
$$G' \sim (1/v)(a/h)^{1/2}(\omega\tau_1)^{1/2}\epsilon_0^{-3/2} \tag{85}$$

Both regimes (3.c and 4.c) are realized when the surface friction is very large, $\tau_1/\tau_0 > (h/a)^4$.

For very large strain amplitude, $\epsilon_0 > \epsilon_{c3}$, we pass to the nonlinear regime 5.c which coincides with regime 3.a for $\omega < \omega^* = \tau_0^{-1}\epsilon_0^2N^{-3}$ and with regime 4.a for $\omega > \omega^*$. The plot of the σ', σ'' vs the strain amplitude ϵ_0 is shown in Figure 4.

The quasi-equilibrium approach is also valid for higher frequencies ($T_1^{-1} < \omega < T_0^{-1}$). The boundary between linear and nonlinear regimes in this intermediate frequency range is $\epsilon_0 \sim h/a$. The whole diagram of regimes is shown in Figure 5. An important feature of the intermediate-frequency range is a sharp change of contribution of the bridges to the stress. If for $\epsilon_0 < h/a$ this contribution is elastic, for larger amplitudes, $\epsilon_0 > h/a$, it becomes dissipative. The stresses and moduli show a pronounced change at the point $\epsilon_0 \sim h/a$, corresponding to a transition from rubberlike to liquidlike behavior. Depending on the imposed frequency, regime 2.c can transform to nonlinear regimes 3.c and 4.c. In the range of the highest frequencies $\tau_1^{-1} < \omega < T_0^{-1}$, there is a direct transition from regime 2.c to regime 4.c. The stress sharply increases at the transition point. If regime 2.c is characterized by elastic behavior with small dissipation, in regime 4.c the system shows liquidlike behavior with small elasticity; therefore, at the transition point σ', G' sharply decrease

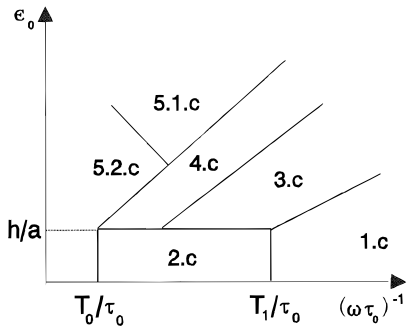

Figure 5. Diagram of regimes in the coordinates $(\epsilon_0; (\omega\tau)^{-1})$ for $(\tau_1/\tau_0 > (h/a)^4, h < aN^{1/2})$.

and, σ'', G'' sharply increase. For frequencies $\tau_1^{-1}(a/h)^{3/2} < \omega < \tau_1^{-1}$, regime 2.c transforms to regime 3.c. As before at the transition point the dissipative stress sharply increases and elastic stress sharply decreases. For low frequencies $\omega < T_1^{-1}$ we have a transition between regimes 1.c and 3.c (at $\epsilon_0 = \epsilon_{c1}$). In this last case there is a continuous transition of the dissipative and elastic stresses. For the strain amplitude $\epsilon_0 \sim \epsilon_{c3}$, we have the second transition point where elastic and dissipative stresses show a jump. This transition is connected with the breakage of all bridges. At this point we have the situation where the dissipative stress sharply decreases. As for elastic stress it also jumps at the transition point, and after this transition, the magnitude of the elastic stress increases, if $(\tau_1/\tau_0) < N^2$ for $(\omega\tau_0)^{-1} > N(h/a)^2$ and $\tau_1/\tau_0 < (h/a)^4(\omega T_0)^{-2}$ for $(h/a)^4 < (\omega\tau_0)^{-1} < N(h/a)^2$, and decreases in the opposite case. These results can be obtained from eqs 31, 32, and 85. Note that in regimes 3.c and 4.c there is a contribution to the stress from the loops. This contribution coincides with that in the linear situation and therefore the moduli are given by eqs 66 and 67.

The scaling dependence of the moduli G' and G'' in the different regimes is the following.

regime 1.c $[\epsilon_0 < \epsilon_{c1};\ \ \omega < T_1^{-1}]$

$$G' \sim \omega^2, \quad G'' \sim \omega \tag{86}$$

regime 2.c $[\epsilon_0 < h/a;\ \ T_1^{-1} < \omega < T_0^{-1}]$

$$G' \sim \omega^0, \quad G'' \sim \omega + \omega^{-1} \tag{87}$$

regime 3.c $[\epsilon_{c1} < \epsilon_0 < \epsilon_{c2}]$

$$G' \sim \epsilon_0^{-2}, \quad G'' \sim \epsilon_0^{-1} \tag{88}$$

regime 4.c $[\epsilon_{c2} < \epsilon_0 < \epsilon_{c3}]$

$$G' \sim \epsilon^{-3/2}\omega^{1/2}, \quad G'' \sim \epsilon_0^{-1/2}\omega^{1/2} \tag{89}$$

regime 5.1.c = regime 3.a $[\epsilon_{c3} < \epsilon_0;\ \ \omega < \omega^*]$

$$G' \sim N\epsilon_0^{-4/3}\omega^{2/3}, \quad G'' \sim \epsilon_0^{-2/3}\omega^{1/3} \tag{90}$$

regime 5.2.c = regime 4.a $[\epsilon_{c3} < \epsilon_0;\ \ \omega > \omega^*]$

$$G' \sim \epsilon_0^{-2/3}\omega^{1/3}, \quad G'' \sim \epsilon_0^{-2/3}\omega^{1/3} \tag{91}$$

2. Weak Surface Friction, $\tau_1/\tau_0 < (h/a)^4$. The contribution of the loops to the dissipative stress becomes more important when $\tau_1/\tau_0 < (h/a)^4$. Regime 4.c does not appear in this situation at all. Analysis shows that in the vicinity of the transition point $\epsilon_0 \sim \epsilon_{c3}$, the contribution of the loops to the dissipative stress is dominant. Here we can separate two situations. The first situation corresponds to the range $(h/a) < \tau_1/\tau_0 < (h/a)^4$. We find a new regime 6.c, where the stresses are determined by the loops and the contribution from the bridges is relatively small. The storage and loss moduli in this regime are determined by the eqs 66 and 67. The line

$$\epsilon_{c4} \sim \left(\frac{a}{h}\right)^3(\omega\tau_0)^{-1} \tag{92}$$

separates the linear regime 6.c from the nonlinear regime 3.c. The elastic and dissipative stresses continue to show a jump at the point $\epsilon_0 \sim h/a$. However, only the elastic stress shows a jump at the point $\epsilon_0 \sim \epsilon_{c3}$ whereas the dissipative stress increases continuously. Thus instead of eqs 88 and 89 we have

regime 3.c $[\epsilon_{c1} < \epsilon_0 < \epsilon_{c4}]$ (bridges)

$$G' \sim \epsilon_0^{-2}, \quad G'' \sim \epsilon_0^{-1} \tag{93}$$

regime 6.c $[\epsilon_{c4} < \epsilon_0 < \epsilon_{c3}]$ (loops)

$$G' \sim \omega^2, \quad G'' \sim \omega \tag{94}$$

In the second case, when $(h/a) > \tau_1/\tau_0$, the bridges are not important any more, and the surface slip becomes dominant. This case is close to the weak adsorption limit with $h > aN^{1/2}$; however, there are several new features. Regime 1.b is transformed into the new regime 1.b′ in which the moduli G' and G'' are given by eq 41 with $N = (h/a)^2$

$$G' \sim (1/\nu)(\omega\tau_1)^2(h/a)^4, \quad G'' \sim (1/\nu)(\omega\tau_1)(h/a) \tag{95}$$

This regime has a boundary with regime 2.b, $\Theta_{b1}^* = (h/a)^4$, and a boundary with regimes 1.b* and 5.b.

$$\epsilon_{b1}^* \sim \Theta(\tau_0/\tau_1)(a/h)^2 \tag{96}$$

The elastic stress and the corresponding storage modulus show a jump (sharply increase) at the point $\epsilon_0 \sim \epsilon_{b1}^*$, and the dissipative stress and the loss modulus transform continuously. For other values of the strain amplitudes and frequencies, the case $\tau_1/\tau_0 < h/a$ coincides with the weak absorption limit for $h > aN^{1/2}$. In the region $(h/a) < \tau_1/\tau_0$ and $\omega > T_0^{-1}$ the behavior of the system coincides with that for the strong adsorption limit with $h > aN^{1/2}$.

IV. Discussion and Conclusions

To conclude, we summarize several important findings which emerge in the nonlinear situation. It is well-known that in the bulk for slow flow, when linear behavior is realized, the relaxation time of the chain conformation is given by the Rouse relaxation time $\tau_0 N^2$. The situation is changed under strong flow conditions. Due to the finite extensibility, the characteristic chain conformation is strongly stretched (non-Gaussian) with reduced normal size $(R_n < aN^{1/2})$. The size depends on the strain rate $\dot{\epsilon}$: $R_n \sim a(\dot{\epsilon}\,\tau_0)^{-1/3}$. The relaxation time can be determined as the chain rotation time: $\tau^* \sim N\tau_0(\dot{\epsilon}\,\tau_0)^{-2/3}$. This time is smaller than the Rouse time. This fact results in the new scaling behavior for the storage

and loss moduli. Thus, for low-frequency nonlinear regime $G' \sim N\epsilon_0^{-4/3}\omega^{2/3}$ and $G'' \sim \epsilon_0^{-2/3}\omega^{1/3}$, and for high frequencies $G' \sim \epsilon_0^{-2/3}\omega^{1/3}$ and $G'' \sim \epsilon_0^{-2/3}\omega^{1/3}$.

The situation becomes more complicated when the effect of the surface slip and the effect of bridges are taken into account. For the weak adsorption limit, the surface slip is important for low frequencies and for not very large strain amplitudes. In the intermediate-frequencies range we find two new scaling regimes for the storage modulus: $G' \sim \omega^{3/2}$ in the linear regime, and $G' \sim \epsilon_0^2\omega^3$ in the nonlinear regime for intermediate strain amplitude. The corresponding boundaries are defined in the section Weak Adsorption Limit.

The effect of the bridges become dominant for low frequencies, when the distance between surfaces $h < aN^{1/2}$. For high surface friction we find jumps in the elastic and dissipative stresses when amplitude $\epsilon_0 \sim h/a$ and $\epsilon_0 \sim \epsilon_{c3}$, where ϵ_{c3} is given by eq 82, at that G'' sharply increases at the point $\epsilon_0 \sim h/a$ and decreases at $\epsilon_0 \sim \epsilon_{c3}$, and therefore passes through a maximum value.

Our results are in a qualitative agreement with experimental findings.[1-9] We note that in some situations the elastic and dissipative stresses show a jump that is in agreement with experiments presented in ref 7. We also show that the loss modulus passes through a maximum when the bridges are important. This fact also agrees with experiment.[9] However, new experiments are necessary for verification of our scaling predictions.

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